



# Quaternized poly(phthalazinone ether ketone ketone) anion exchange membrane with low permeability of vanadium ions for vanadium redox flow battery application

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## HIGHLIGHTS

- CMPPEKK was first prepared with nitrobenzene as solvent.
- QAPPEKK membrane showed low vanadium ions permeability.
- QAPPEKK membrane in VRB showed high columbic efficiency.
- QAPPEKK membrane was stable in  $\text{VO}_2^+$  electrolyte.
- QAPPEKK membrane showed stable performance in VRB cycling test.

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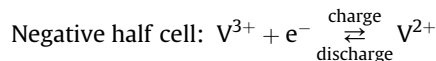
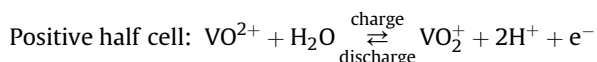
## ABSTRACT

To develop cost-effective membranes with low permeability of vanadium ions for vanadium redox flow battery (VRB) application, an inexpensive precursor membrane material, chloromethylated poly(phthalazinone ether ketone ketone), is first prepared from poly(phthalazinone ether ketone ketone) with nitrobenzene as the solvent, and then reacted with trimethylamine to form quaternized poly(phthalazinone ether ketone ketone) (QAPPEKK) anion exchange membranes. At an ion exchange capacity of  $1.56 \text{ mmol g}^{-1}$ , the QAPPEKK membrane shows much lower permeability of vanadium ions ( $0.17 \times 10^{-4} \text{ cm min}^{-1}$  for  $\text{V}^{3+}$  and  $0.21 \times 10^{-4} \text{ cm min}^{-1}$  for  $\text{VO}^{2+}$ ) than that of Nafion117 membrane ( $1.34 \times 10^{-4} \text{ cm min}^{-1}$  for  $\text{V}^{3+}$  and  $1.19 \times 10^{-4} \text{ cm min}^{-1}$  for  $\text{VO}^{2+}$ ), resulting in higher coulombic efficiency (99.4% at  $80 \text{ mA cm}^{-2}$ ). In addition, the energy efficiency of the VRB with QAPPEKK membrane is comparable to that of VRB with Nafion117 membrane. Moreover, the QAPPEKK membrane is stable in  $\text{VO}_2^+$  electrolyte, and exhibits good performance in the 100-cycle charge-discharge test of VRB.

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## 1. Introduction

Vanadium redox flow battery (VRB) reported by M. Skyllas-Kazacos and coworkers [1] is a novel energy storage system. The half-cell electrode reactions as follows:



VRB has received considerable attention in recent years due to its flexibility in design and facility to regenerate the electrolyte solution. As one of the key components of VRB, ion exchange membrane is used to prevent cross mixing of the positive and negative electrolytes and allow the transport of ions to complete the circuit during the passage of current [2]. The ideal ion exchange membrane for VRB should have high ion conductivity, low permeability of vanadium ions, and good stability. Nafion membrane has been investigated for VRB application owing to its high proton conductivity and good chemical stability. However, Nafion membrane is limited in commercial application in VRB due

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to its high cost and high permeability of vanadium ions. To reduce the permeability of vanadium ions through Nafion membrane, many attempts have been carried out. Representative works include Nafion/SiO<sub>2</sub> hybrid membrane, Nafion/organic silica modified TiO<sub>2</sub> composite membrane, self-assembled poly-electrolyte multilayer modified Nafion membrane, and interfacial polymerization modified Nafion membrane [3–6].

Besides Nafion platform, many alternative cation and anion exchange membranes were reported in VRB applications, such as poly (vinylidene difluoride) membrane, poly (ethylene-co-tetrafluoroethylene) membranes, sulfonated poly(flourenyl ether ketone) membrane, sulfonated poly(tetramethyldiphenyl ether ether ketone) membrane, and sulfonated poly(ether ether ketone) based multilayered membrane [7–11]. Compared with cation exchange membrane, anion exchange membrane enjoys lower permeability of vanadium ions owing to the Donnan exclusion effect between anion exchange groups and vanadium ions [12–17]. In this work, we report the quaternized poly(phthalazinone ether ketone ketone) (QAPPEKK) anion exchange membranes for VRB application.

Poly(phthalazinone ether)s were a series of high performance aromatic polymer materials. In our previous reports, chloromethylated poly(phthalazinone ether)s were prepared by using concentrated sulfuric acid (95–98%) as solvent and used to make anion exchange membranes for VRB applications [15–19]. Here, a more environmental friendly solvent was utilized to prepare the chloromethylated poly(phthalazinone ether ketone ketone) (CMPPEKK), which avoided the generation of much acidic wastewater, and the reaction solvent can be recycled. The properties of resulting quaternized poly(phthalazinone ether ketone ketone) (QAPPEKK) membranes in VRB single cell were evaluated, including the stability of membrane in VO<sub>2</sub><sup>+</sup> electrolyte and charge-discharge cycle performance of VRB with QAPPEKK membrane.

## 2. Experimental

### 2.1. Materials

Poly(phthalazinone ether ketone ketone) (PPEKK) polymer was synthesized in our lab according to the procedure described previously [20]. Chloromethyl methyl ether (CME) (Shanghai Haiqu

Chemical Company), aluminium chloride anhydrous (AlCl<sub>3</sub>) (Tianjin Bodi Chemical Co., Ltd), vanadyl sulfate (VOSO<sub>4</sub>) (Shanghai Luyuan Fine Chemical Plant), trimethylamine solution (33 wt.%) (Tianjin Guangfu fine chemical research institute) and other chemicals were commercially obtained and used as received.

### 2.2. Chloromethylation of PPEKK

PPEKK (5.2 g) was dissolved in nitrobenzene (50 mL) in a flask equipped with mechanical stirring and a condenser, followed by adding AlCl<sub>3</sub>. After the AlCl<sub>3</sub> was dissolved completely, chloromethyl methyl ether was added dropwise, and the solution was heated to 60 °C. After 3 h, the solution was cooled and poured into 5 wt.% HCl. After washed with ethanol, the obtained polymer was dried at 60 °C under vacuum for 48 h. The chemical structure and the degree of chloromethylation (DCM) of resulting polymer were determined by <sup>1</sup>H NMR (Bruker AvanceII400M) measurement. The degree of substitution (DS) of CMPPEKK was defined as the number of chloromethyl groups per polymer repeat unit. The degree of chloromethylation (DCM) of CMPPEKK was evaluated by the following equation [16]:

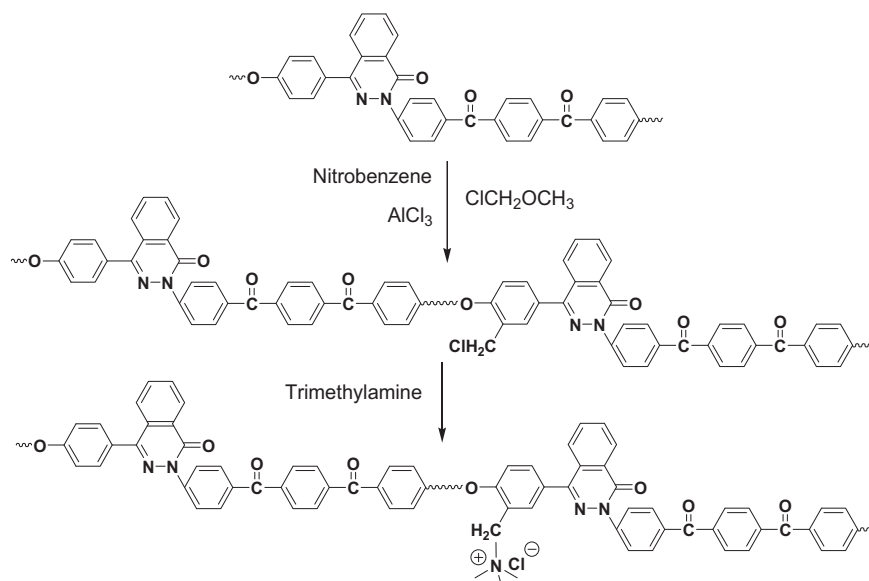
$$\text{DCM (mmol/g)} = \frac{\text{DS} \times 1000}{520.53 + \text{DS} \times 48.48}$$

### 2.3. Preparation of membrane

Chloromethylated polymer was dissolved in *N*-methyl-2-pyrrolidone to form a 10 wt.% casting solution, and then the solution was casted onto a smooth glass plate at 60 °C to obtain a base membrane. The base membrane was soaked in trimethylamine solution (33 wt.%) at 40 °C for 48 h to obtain quaternized membrane (Scheme 1). After that, the membrane was immersed into 5 wt.% HCl to neutralize residual trimethylamine, and then washed with excess deionized water to remove residual HCl.

### 2.4. Characterization of membrane

The ion exchange capability (IEC) of membrane was determined by titration. A dried QAPPEKK membrane (in chloride form) was obtained under vacuum at 60 °C for 48 h, and then it was weighed



Scheme 1. Synthesis of QAPPEKK.

and immersed in 25 mL 0.1 mol L<sup>-1</sup> NaNO<sub>3</sub> solution for 48 h at room temperature. After that the solution was back titrated with 0.1 mol L<sup>-1</sup> AgNO<sub>3</sub>, and K<sub>2</sub>CrO<sub>4</sub> was employed as indicator. IEC was calculated according to the following equation:

$$\text{IEC} = \frac{V_{\text{AgNO}_3} \times C_{\text{AgNO}_3}}{M}$$

where  $V_{\text{AgNO}_3}$  was the volume of AgNO<sub>3</sub> solution,  $C_{\text{AgNO}_3}$  was the concentration of AgNO<sub>3</sub> solution, and  $M$  was the weight of dried membrane, respectively. For each measurement, the presented results were averages of three samples.

Water uptake of QAPPEKK membrane was determined by equilibrating the sample of membrane with deionized water at room temperature for 24 h. The membrane was wiped using absorbent paper and weighed immediately. Then the membrane was dried at 60 °C under vacuum for 48 h. Water uptake was calculated according to the following equation:

$$\text{Water uptake(\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  were the weights of the membrane in wet and dry state, respectively. For each measurement, the presented results were averages of three samples.

To evaluate the swelling ratio of the QAPPEKK membranes in deionized water and vanadium electrolyte, membrane samples were dried at 60 °C under vacuum for 48 h, and then the length of membrane were measured. After that the membranes were soaked in deionized water and 1.5 mol L<sup>-1</sup> V(IV) solution for 24 h, respectively. A 1.5 mol L<sup>-1</sup> V(IV) solution was prepared by dissolving 1.5 mol VOSO<sub>4</sub> in 3 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. The swelling ratio was calculated according to the following equation:

$$\text{Swelling ratio} = \frac{L_1 - L_0}{L_0} \times 100\%$$

where  $L_1$  and  $L_0$  were the length of the soaked membrane and dry membrane, respectively. For each measurement, three samples were prepared, and the presented results were averages.

Area resistance ( $R$ ) of the QAPPEKK membranes was evaluated by the method described in literature [19,21]. The detail procedure was as follows: 2 mol L<sup>-1</sup> VOSO<sub>4</sub> in 3 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution for the measurement was prepared by dissolving 2 mol VOSO<sub>4</sub> in 3 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. Before the test, the sample of membrane was soaked in a solution of 2 mol L<sup>-1</sup> VOSO<sub>4</sub> in 3 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solution for 24 h. And then the membrane was fixed between two half-cells containing a 1.0 cm diameter hole. Each half-cell was filled with 2 mol L<sup>-1</sup> VOSO<sub>4</sub> in 3 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solution. The resistances with membrane ( $r_1$ ) and without membrane ( $r_2$ ) were measured at 25 °C via CHI660C electrochemistry working station with impedance technique. The frequency range was 1 Hz to 1 MHz, the effective membrane area  $S$  of the cell was 0.79 cm<sup>2</sup>. The area resistance ( $R$ ) of the membrane was calculated by the following equation:  $R = (r_1 - r_2) \times S$ . For each measurement, three samples were prepared, and the presented results were averages.

Mechanical properties of membrane were tested on INSTRON 5567A at 20 °C with 50% relative humidity. And, the cross-head speed was 2 mm min<sup>-1</sup>. The size of sample was 6 mm × 50 mm. For each measurement, five samples were prepared, and the presented results were averages.

The permeations of VO<sup>2+</sup> and V<sup>3+</sup> through membrane were evaluated by the methods described in literature [15,22]. The membrane was sandwiched between two half-cells. One half-cell was filled with a vanadium solution, and the other was filled with a solution of 1.0 mol L<sup>-1</sup> MgSO<sub>4</sub> in 2.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

1.0 mol L<sup>-1</sup> VOSO<sub>4</sub> in 2.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> was prepared by dissolving VOSO<sub>4</sub> in 2.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, while V(III) solutions were obtained by electrochemical reduction of the V(IV) solution. MgSO<sub>4</sub> was used to balance the ionic strength and minimize the osmotic pressure between the two solutions. Area of the membrane exposed to the solution was 1.76 cm<sup>2</sup> and volume of solutions in both half-cells was 30 mL. The concentration of vanadium ion in MgSO<sub>4</sub> solution was determined periodically by using a UV/Vis spectrophotometer. The wavelengths for V<sup>3+</sup> and VO<sup>2+</sup> were 605.0 nm and 765.5 nm, respectively. The V(II) and V(V) solutions were not taken for analysis, since V(II) solution was unstable in air and the light absorption of VO<sub>2</sub><sup>+</sup> was so weak during the wavelength region available by the UV/Vis spectrometer [23]. The rate of change in the solution absorbance is used to calculate the diffusion coefficient for the vanadium ion according to the Fick's First Law and Beer's Law. Diffusion coefficient ( $K_s$ ) was obtained by the following relationship:

$$\ln[\text{absB}_0 - 2\text{absA}] = \ln[\text{absB}_0] - 2K_s t / V_A$$

where  $\text{absB}_0$  is the initial absorbance of solution B (i.e. VO<sup>2+</sup> solution),  $\text{absA}$  is the absorbance of solution A (i.e. MgSO<sub>4</sub> solution),  $A$  is the area of membrane exposed to the solution,  $V_A$  is the volume of solution A,  $t$  is the interval time. The diffusion coefficient  $K_s$  obtained by the slope of the straight line of ( $\ln[\text{absB}_0 - 2\text{absA}]$  vs.  $t$ ). For each measurement, two samples were prepared, and the presented results were averages.

The cell test was according to the methods described in literature [16,21]. The membrane was sandwiched between two pieces of carbon felts, and two pieces of graphite plates were served as current collectors. At the beginning of cell test, the negative electrolyte and positive electrolyte were 1.5 mol L<sup>-1</sup> V(III) in 3.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 1.5 mol L<sup>-1</sup> VOSO<sub>4</sub> in 3.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, respectively. Electrolytes were stored separately in two tanks and the volume of electrolytes was 30 mL for each. During the cell test, the positive electrolyte and negative electrolyte were pumped into the positive and negative compartments of the cell, respectively. The effective area of membrane was 5 cm<sup>2</sup>. The cell was charged and discharged using a battery test system CT-3008-5V/3A (Neware Co., Ltd, China), and the upper limit of charge voltage and lower limit of discharge were 1.8 V and 0.8 V, respectively. The stability of QAPPEKK membrane was evaluated by immersing the membranes in 1.5 mol L<sup>-1</sup> VO<sub>2</sub><sup>+</sup> in 3 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution for 30 days, and then its performance in VRB single cell was tested.

### 3. Results and discussion

#### 3.1. Preparation of QAPPEKK membrane

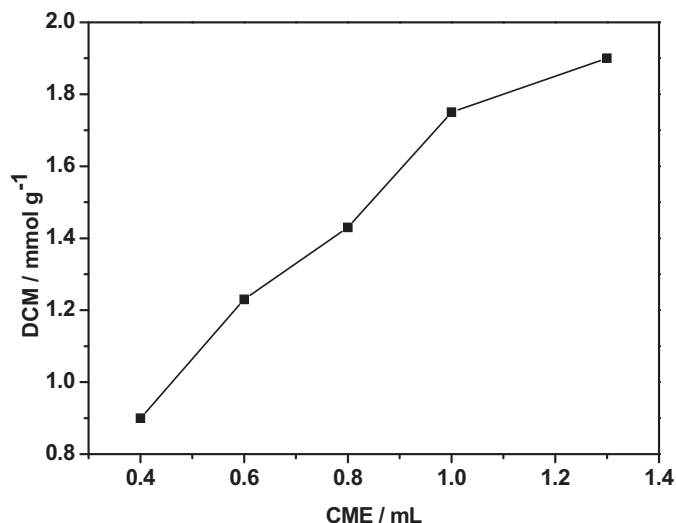
##### 3.1.1. Chloromethylation of PPEKK

In our previous reports [16–19], chloromethylated poly(-phthalazinone ether)s were prepared by using concentrated sulfuric acid (95–98%) as both catalyst and solvent. However, the concentrated sulfuric acid is highly corrosive and cannot be recycled after the reaction, and considerable amount of acidic

**Table 1**

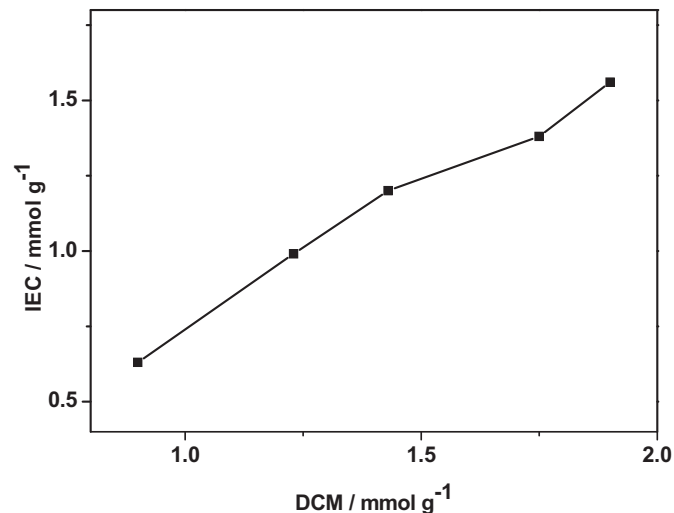
Effect of AlCl<sub>3</sub> quantity on the DCM of CMPPEKK: nitrobenzene was 50 mL; reaction time was 3 h; reaction temperature was 60 °C; PPEKK was 5.2 g; CME was 1.0 mL.

Code	AlCl <sub>3</sub> (mol)	DCM (mmol g <sup>-1</sup> )
1	0.03	0.69
2	0.04	1.66
3	0.05	1.75
4	0.10	1.71
5	0.15	1.62



**Fig. 1.** Effect of chloromethyl methyl ether (CME) quantity on DCM of CMPPEKK: PPEKK was 5.2 g; nitrobenzene was 50 mL;  $\text{AlCl}_3$  was 0.05 mol; reaction temperature was 60 °C; reaction time was 3 h.

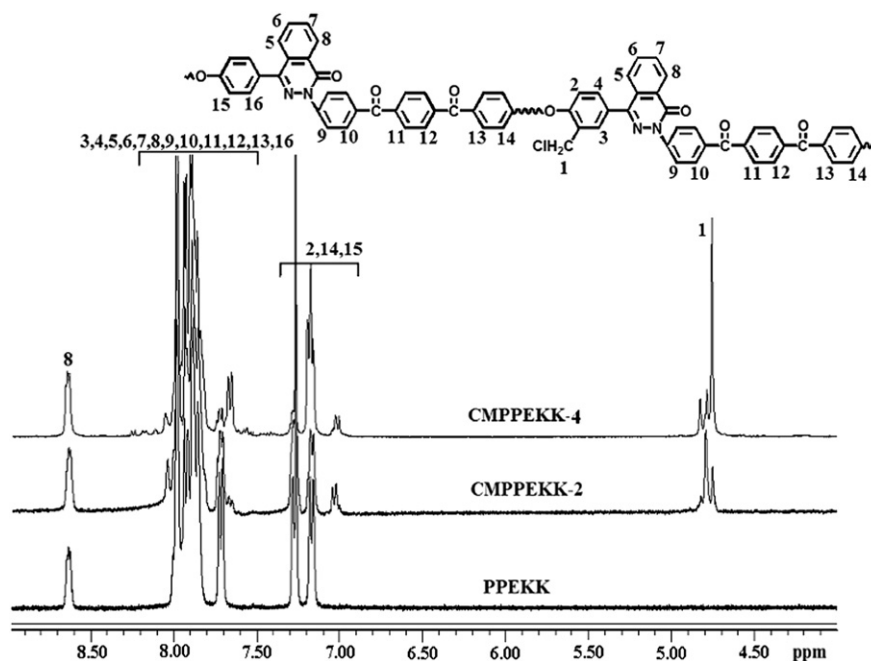
wastewater was produced. Herein, we switched to nitrobenzene as solvent (Scheme 1). The generation of acidic wastewater can be avoided and the solvent could be recycled. Firstly, the effects of amounts of  $\text{AlCl}_3$  and chloromethyl methyl ether (CME) on degree of chloromethylation (DCM) of CMPPEKK were investigated.  $\text{AlCl}_3$  is widely applied as low-cost Lewis acid catalyst for Friedel–Crafts alkylation. The effects of  $\text{AlCl}_3$  quantity on DCM of CMPPEKK were listed in Table 1. With 0.05 mol of  $\text{AlCl}_3$ , the highest DCM of 1.75  $\text{mmol g}^{-1}$  was obtained. However, further increase of the amount of catalyst depressed the DCM, and at 0.15 mol of catalyst loading small fraction of gelation occurred. Clearly, excess catalyst will cause the side reaction. Therefore, the optimum amount of  $\text{AlCl}_3$  was 0.05 mol for the reaction. As shown in Fig. 1, there was a linear relationship between the amount of CME and DCM of



**Fig. 3.** Effect of DCM on IEC of QAPPEKK membranes.

CMPPEKK during the test range. The DCM can reach 1.90  $\text{mmol g}^{-1}$  without gelation of the polymer at 1.3 mL of CME loading. The result indicated that the DCM value can be easily tailored via changing the amount of CME.

As mentioned in the experimental part,  $^1\text{H}$  NMR measurement was employed to calculate the degree of substitution (DS) of CMPPEKK. In the  $^1\text{H}$  NMR spectrum of CMPPEKK (Fig. 2), a new peak at 4.75 ppm was assigned to the methylene protons in the chloromethyl groups [15,16,19], and its integral area was enhanced with an increase of DCM. The DS of CMPPEKK was defined as the number of chloromethyl groups per polymer repeat unit. Therefore, DS was estimated from the integral ratio of  $-\text{CH}_2\text{Cl}$  (H1) at 4.75 ppm to the protons at 8.62 ppm (H8) which were intact during the chloromethylation reaction [16,18], and the calculation equation was shown as following:



**Fig. 2.**  $^1\text{H}$  NMR spectra of PPEKK and CMPPEKK in  $\text{CDCl}_3$ .

**Table 2**  
Properties of membranes.

Membrane	IEC (mmol g <sup>-1</sup> )	Water uptake (%)	R (Ω cm <sup>2</sup> )	Swelling ratio (%)		Tensile strength (MPa)	Elongation at break (%)	Thickness (μm)
				H <sub>2</sub> O	Vanadium electrolyte			
QAPPEKK-1	0.99	11.5	1.69	5.2	4.5	38	35	44
QAPPEKK-2	1.20	16.5	1.31	7.8	6.3	34	31	45
QAPPEKK-3	1.38	18.4	0.64	8.4	7.2	35	42	44
QAPPEKK-4	1.56	20.8	0.57	12.2	11.2	40	35	50

$$DS = \frac{1/2 A_1}{A_8}$$

where  $A_1$  was the integration value of H1,  $A_8$  was the integration value of H8, respectively.

### 3.1.2. QAPPEKK membrane

After immersed CMPPEKK membranes into trimethylamine solution, the resulting quaternized membranes were soaked with 5 wt.% HCl to neutralize residual trimethylamine, and then washed with deionized water to remove residual HCl. As shown in Fig. 3, IEC value increased proportionally with the increase of DCM, which indicated the quaternary ammonium groups were successfully prepared as we expected.

### 3.2. Properties of membrane

The properties of QAPPEKK membranes including water uptake, area resistance, swelling ratio, and mechanical strength were summarized in Table 2. Water uptake is one of basic parameters of ion exchange membrane. An appropriate amount of water uptake enables the membrane to achieve both good ion conductivity and mechanical property. Excessive water uptake of the membrane will result in severe swelling and deteriorate dimensional stability, and even leads to the loss of the mechanical properties. Basically, water uptake of anion exchange membrane is strongly dependent upon the amount of quaternary ammonium groups, which is related to the IEC values. In our case, water uptake of the QAPPEKK membranes was in the range of 11.5–20.8%.

The membranes were soaked in a solution of 2 mol L<sup>-1</sup> VOSO<sub>4</sub> in 3 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solution for 24 h before measuring their area resistances. As shown in Table 2, area resistances ( $R$ ) of the

membranes were reduced with the increase of IEC. Among the obtained QAPPEKK membranes, the QAPPEKK-4 membrane had the highest IEC value and the lowest area resistance of 0.57 Ω cm<sup>2</sup>, which was close to Nafion117 membrane (0.54 Ω cm<sup>2</sup>) [15]. With respect to the swelling ratio of QAPPEKK membranes, this value was determined as a function of IEC in both deionized water and VOSO<sub>4</sub> solution. For the detail, the swelling ratio of QAPPEKK in deionized water ranged from 5.1 to 12.2 %, whereas it ranged from 4.5 to 11.2 % in VOSO<sub>4</sub> solution. The value in water swelling was slightly higher than that in VOSO<sub>4</sub> solution because swelling ratio depended on the osmotic pressure difference between the external solutions and internal solutions of the membrane, and the osmotic pressure difference is larger in deionized water than in VOSO<sub>4</sub> solution [24].

In VRB, one of the functions of membrane was to separate the positive electrolyte and negative electrolyte which was continuously pumped through the positive half-cell and negative half-cell, respectively. Therefore, the membrane was required to have good mechanical stability. As shown in Table 2, the tensile strength and elongation at break of QAPPEKK membranes were higher than 30 MPa and 30%, respectively, which indicated that QAPPEKK membrane could be a promising ion exchange membrane for VRB application. In the following experiment, QAPPEKK-4 membrane was chosen to test the permeability and VRB single cell performance since the membrane showed the lowest area resistance and would have the best performance in VRB among QAPPEKK membranes.

### 3.3. Permeability of vanadium ions through Nafion117 membrane and QAPPEKK membrane

The permeability of V(III) and V(IV) through Nafion117 membrane and QAPPEKK-4 membrane were measured and the results were summarized in Fig. 4. It is clear that both the permeability of V(III) and V(IV) ions were depressed greatly in QAPPEKK membrane compared to Nafion117 membrane. The reason for this was that QAPPEKK membrane with quaternary ammonium groups has Donnan exclusion effect between positively charged ion exchange groups and vanadium ions. This effect enables QAPPEKK membrane to have lower permeability of vanadium ions than that of Nafion117 membrane [16]. The diffusion coefficients  $K_s$  were obtained by the slope of the straight line of ( $\ln [\text{absB}_0 - 2\text{absA}]$  vs.  $t$ ). And the calculation results listed in Table 3 indicated that the  $K_s$  values for V(III) and V(IV) in QAPPEKK-4 membrane reduced to

**Table 3**  
Vanadium ion permeability of Nafion117 and QAPPEKK-4 membrane.

Membrane	IEC (mmol g <sup>-1</sup> )	Vanadium ion permeability $K_s (\times 10^{-4} \text{ cm min}^{-1})$	
		V(III)	V(IV)
Nafion117	0.91	1.34	1.19
QAPPEKK-4	1.56	0.17	0.21

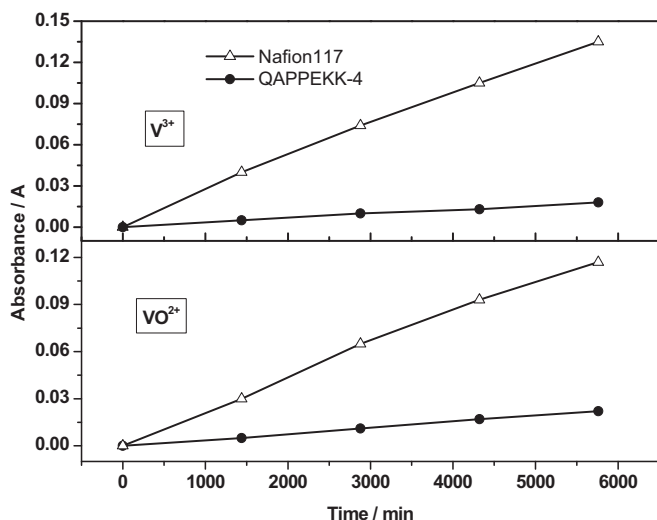


Fig. 4. Absorbance value of vanadium ions in MgSO<sub>4</sub> solution.



about one eighth and one sixth of those in Nafion117 membrane, respectively. These results illuminated that VRB with QAPPEKK membrane would have a higher coulombic efficiency than that of VRB with Nafion117 membrane.

### 3.4. Vanadium redox flow battery (VRB) performance

The typical charge–discharge curves of VRB with QAPPEKK-4 and Nafion117 membrane were outlined in Fig. 5. The VRB with former membrane showed higher average charge voltage and lower average discharge voltage, this was caused by the higher area resistance of QAPPEKK membrane than Nafion117 membrane [10]. The charge capacity and discharge capacity of the VRB with QAPPEKK membrane were lower than that with Nafion117 membrane, since the higher area resistance of QAPPEKK membrane resulted in higher IR drop and reduced the charge capacity and discharge capacity of the VRB single cell.

The effects of current density on VRB single cell efficiency of the VRB with Nafion117 membrane and QAPPEKK membrane were illustrated in Fig. 6. As shown, the current efficiency (CE) of VRB increased with the increase of charge–discharge current density. For all range of charge–discharge current densities, the CE of VRB with QAPPEKK was higher than that of VRB with Nafion117 membrane. The reason was that QAPPEKK membrane has lower permeability of vanadium ions than Nafion117 membrane. The VRB single cell with QAPPEKK membrane showed a CE of 97.8% at a low current density of  $20 \text{ mA cm}^{-2}$ , and it delivered a CE of 99.4% when the current density was increased to  $80 \text{ mA cm}^{-2}$ . On the other hand, when the current density increased from 20 to  $80 \text{ mA cm}^{-2}$ , the CE of VRB single cell with Nafion117 membrane increased only from 94.2 to 96.8%. The voltage efficiency (VE) of the VRB with Nafion117 membrane and QAPPEKK membrane all decreased with the charge–discharge current densities. It is due to the increase of ohmic resistance and the overpotentials led by the increase of current densities [25]. It was noted that VE of VRB with QAPPEKK membrane was lower than that of VRB with Nafion117 membrane, especially at higher current densities ( $\geq 50 \text{ mA cm}^{-2}$ ). This may be attributed to the Donnan exclusion effect between quaternized ammonium groups and protons that the ion conductivity of membrane decreased more considerably at higher current densities. Therefore, to further enhance the performance of VRB, improvement of ion conductivity of QAPPEKK membrane especially at high current density is required. Energy efficiency (EE) of both

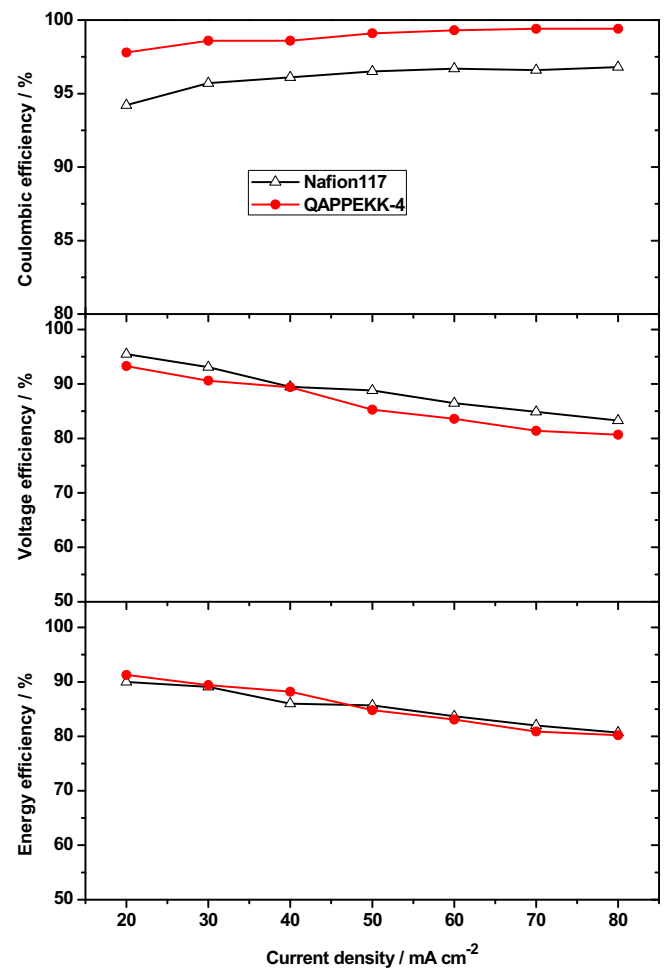


Fig. 6. Effect of current density on coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) of the VRB with Nafion117 and QAPPEKK-4 membrane, respectively.

VRB with QAPPEKK membrane and VRB with Nafion117 membrane decreased with the increase of current densities, and the energy efficiency of both cells was comparable. It showed a maximum EE of the VRB, which was 91.3% for QAPPEKK and 89.9% for Nafion117

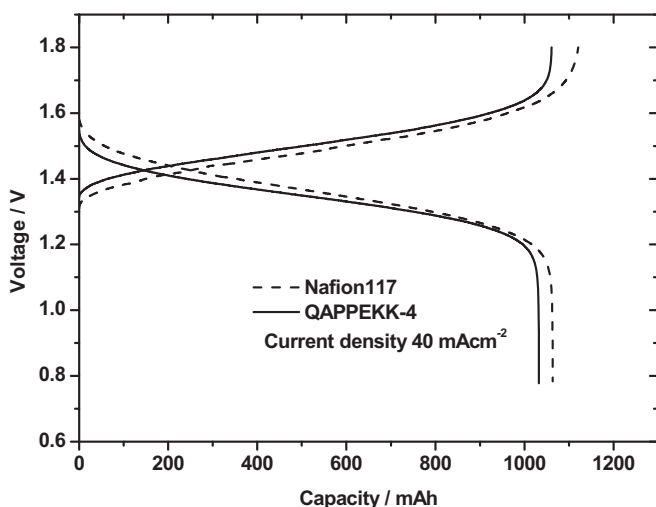


Fig. 5. Charge–discharge curves for VRB with Nafion117 and QAPPEKK-4 membrane at  $40 \text{ mA cm}^{-2}$ .

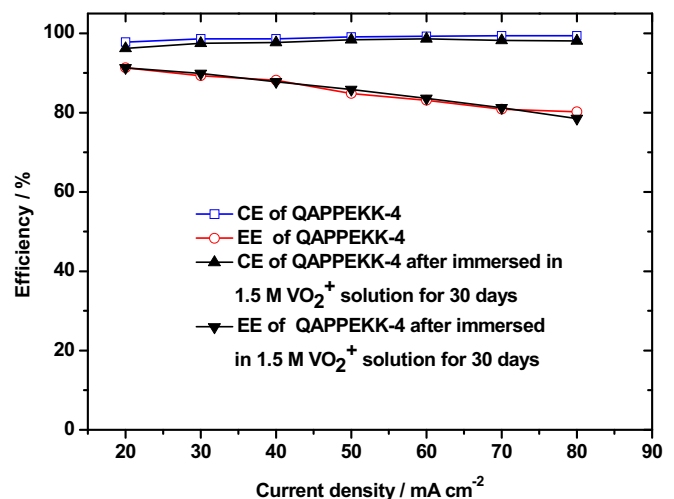


Fig. 7. Effect of charge–discharge current density on coulombic efficiency (CE) and energy efficiency (EE) of the VRB with QAPPEKK membrane before and after immersed in  $\text{VO}_2^+$  solution for 30 days, respectively.

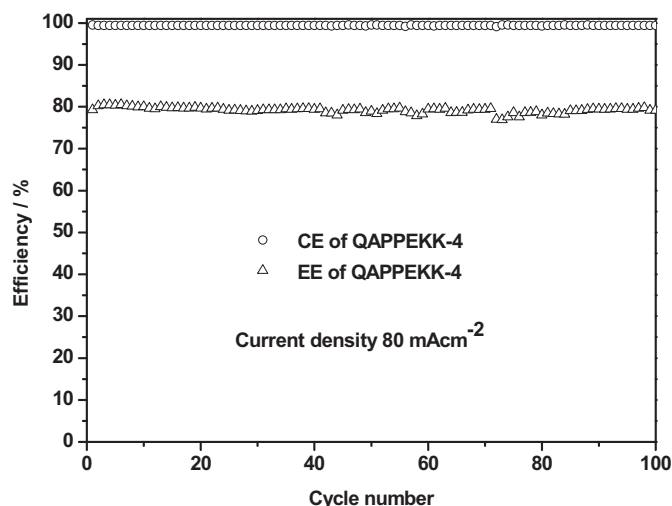


Fig. 8. Charge-discharge cycling performance ( $80 \text{ mA cm}^{-2}$ ) of VRB with QAPPEKK membrane.

membrane at  $20 \text{ mA cm}^{-2}$ . It also showed a minimum EE of the VRB, which was 80.2% for QAPPEKK and 80.7% for Nafion117 membrane at  $80 \text{ mA cm}^{-2}$ . The results of VRB single cell performance test suggested that the low-cost QAPPEKK membrane could be a promising alternative ion exchange membrane for Nafion117 membrane.

### 3.5. Stability test of membrane

Stability of the alternative membrane is a critical issue for VRB. To evaluate the stability of QAPPEKK membrane in  $\text{VO}_2^+$  electrolyte, QAPPEKK-4 membrane was immersed in  $1.5 \text{ mol L}^{-1} \text{VO}_2^+$  in  $3 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  for 30 days at room temperature, then the performance of VRB single cell with the membrane was tested. As shown in Fig. 7, there was no significant change in CE and EE before and after immersed the membrane in  $\text{VO}_2^+$  solution, which indicated that the QAPPEKK membrane was endurable in oxidative  $\text{VO}_2^+$  electrolyte.

In order to further investigate the stability of QAPPEKK membrane in VRB, the cycle performance of VRB with QAPPEKK membrane at a charge-discharge current density of  $80 \text{ mA cm}^{-2}$  was tested. As showed in Fig. 8, the CE and EE remained about 99% and 80%, respectively, after 100 cycles, which suggested that QAPPEKK membrane was stable in VRB. For practical application, the stability test merely based on soaked in  $\text{VO}_2^+$  solution for 30 days or 100-cycles test was insufficient, therefore, a longer term cycling test with QAPPEKK membrane is underway in our lab.

## 4. Conclusions

Quaternized poly(phthalazinone ether ketone ketone) membranes were prepared and their properties were investigated for vanadium redox flow battery (VRB) applications. Chloromethylated poly(phthalazinone ether ketone ketone) was first prepared from poly(phthalazinone ether ketone ketone) with

nitrobenzene as the solvent. The properties of resulting quaternized poly(phthalazinone ether ketone ketone) (QAPPEKK) anion exchange membranes were investigated. The QAPPEKK membrane had significantly lower permeability of vanadium ions than Nafion117 membrane, and improved coulombic efficiency in VRB single cell tests. Ks values for V(III) and V(IV) in QAPPEKK-4 membrane were reduced to about one eighth and one sixth of those in Nafion117 membrane, respectively. At  $80 \text{ mA cm}^{-2}$ , 99.4% coulombic efficiency was achieved with the QAPPEKK membrane, compared to 96.8% with Nafion117 membrane, and the energy efficiency of both cells was comparable. The results of stability test indicated that QAPPEKK membrane was stable in  $\text{VO}_2^+$  electrolyte, and the 100-cycle charge-discharge performance of VRB with QAPPEKK membrane exhibited stable performance. The QAPPEKK membrane showed advantageous performance attributes in VRB tests, but improvement of the ion conductivity of membranes at high charge-discharge current density is required.

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